Pseudospectral contracted configuration interaction from a generalized valence bond reference

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(Received 28 March 1994; accepted 29 April 1994)

A multireference configuration interaction method is presented based upon pseudospectral integration and a novel generalized valence bond referenced contraction procedure. The combination of these approaches is shown to allow for unprecedented multiconfiguration self-consistent-field calculations on large molecules.

I. INTRODUCTION

Substantial progress has been made in the development of accurate self-consistent multiconfigurational (MCSCF) wave functions.[1] In particular, it has been shown that multireference CI (MRCI)[2] and more recently multireference perturbation theory (MRPT)[3–6] using these MCSCF references leads to quite accurate predictions for a wide variety of molecular properties. However, the computational cost of these MCSCF based methods grows very quickly with the size of the molecule thus limiting studies at the MRCI or multiconfigurational perturbation theory level to the order of 10 to 20 electrons. The two computational bottlenecks of conventional methods which have prevented the applications of highly correlated methods to large molecules are the unfavorable scaling with basis size of the two-electron integral evalution over orbitals and the rapid growth in the length of the multiconfigurational expansion with the number of active orbitals.

In this paper we present new methods for significantly reducing the cost of two-electron integral evaluation via pseudospectral integration techniques and a novel contraction procedure for reducing the length of CI expansions generated from a generalized valence bond (GVB) reference. These two techniques introduce the possibility of correlated calculations of unprecedented size.

The pseudopsectral integration method, developed by Friesner and co-workers,[7–12] uses a Gaussian basis set and a numerical grid together to obtain two-electron integrals each involving four functions, two active orbitals, and two basis functions. For N_{bas} basis functions this procedure scales as N_{bas}^3 as compared to the conventional N_{bas}^4 scaling of evaluating integrals over basis functions. Furthermore, a fast two-index transform of the pseudopsectral integrals gives the necessary integrals over orbitals for a CI calculation. In contrast, the conventional methodology requires an expensive (N_{bas}^5 process) four-index transform from the basis set to the orbital space. The pseudospectral integration method, while an approximation to the conventional analytic integration, has been shown[11] to give total electronic energies to within 0.1 kcal/mol of conventional methods for Hartree–Fock and GVB wave functions. We show here that the same accuracy is obtainable for a MRCI wave function constructed from a GVB reference.

The correlated wave function we develop here is constructed from intrapair excitations of a GVB perfect pairing (GVB-PP) reference wave function where perfect pairing refers to the use of a single valence bond spin coupling among pairs of bonded orbitals. This so-called "restricted CI" (RCI) wave function uses an active-orbital space of the two natural orbitals of each GVB-PP pair. The RCI wave function in what will be referred to as its "uncontracted" form was first considered by Harding and Goddard.[13] The RCI wave function, though less complete than a complete-active-space (CASSCF)[14,15] expansion defined in the same active orbital space, has been shown[4,5,16] to give energies and properties when used as a reference for subsequent MRCI or MRPT which are nearly the same as those obtained with a CASSCF reference.

Although the uncontracted RCI wave function contains fewer configurations and is hence more manageable than a CASSCF expansion, the length of this expansion grows beyond a million configurations for 20 electrons. The key to making the RCI expansion tractable for large systems is shown here to lie in the structure of the multiconfigurational GVB-PP reference wave function. The spatial part of the GVB-PP wave function is defined as a single product of pairwise overlapping local orbitals. Each pair of bonded local orbitals is expressed as a linear combination of mutually orthogonal local natural orbitals with the two coefficients of this nonorthogonal to orthogonal transformation being variational parameters. In the natural orbital basis the wave function describing N GVB pairs is an expansion in 2^N closed-shell deteminants. However, the CI coefficients of this expansion are functionals of the $2N$ orbital coefficients defining the transformation from the local overlapping GVB orbitals to the orthogonal natural orbitals. Therefore, the GVB-PP wave function represents a contracted CI expansion in which the contraction is defined by the shapes of the local orbitals. For a large number of pairs, the calculation of the $2N$ orbital coefficients[17] is far simpler than diagonalization

 0021-9606/94/101(4)/2986/9/$6.00

of a large 2^N dimensional matrix. Most importantly, the GVB-PP energy is within 0.02 kcal/mol of the fully variational 2^N configuration CI for a series of small molecule test cases we have examined.

In this paper we extend this orbital based contraction to the RCI wave function, and in principle, to more general MRCI and MRPT expansions from a reference expressed in terms of GVB pairs. The RCI contraction procedure consists of two parts. First, the RCI expansion is defined by making excitations from the orbital contracted, multiconfigurational GVB-PP expansion rather than by making excitations of the individual 2^N configurations contained in the GVB expansion. This definition is analogous to the MRCI contraction procedure commonly used[2] by other authors, with the new aspect that the reference itself is also contracted. Each variationally weighted RCI configuration is a sum of many uncontracted configurations, Second, as with GVB-PP, the RCI CI coefficients are functionals of the GVB-PP pair coefficients. As demonstrated below, this contraction procedure leads to very large reductions in the size of the CI matrix with little loss in accuracy relative to the corresponding uncontracted expansion. Furthermore, matrix elements among contracted RCI configurations are easily evaluated by replacing the common unexcited GVB-PP pairs of interacting configurations by a generalized Fock operator representing the mean field of the unexcited GVB-PP pairs. This correlated mean field replaces a large fraction of the two-electron matrix elements by a rapidly evaluated single-particle operator.

We develop in some detail the contracted pseudospectral RCI wave function outlined above. Examples of the high accuracy of the contraction approximation relative to the uncontracted CI are provided. Pseudospectral integration is shown to cause negligible errors relative to conventional analytic integration. Finally, we present test calculations on diatomic molecules and CPU timings for larger molecules.

II. GVB REFERENCE WAVE FUNCTION

We first discuss the GVB reference wave function to point out the computational efficiencies of this multiconfigurational expansion and to motivate the use of these efficiencies in constructing correlated wave functions from a GVB reference. A more extensive discussion of the optimization of GVB-PP wave functions can be found in Ref. 17. The reference GVB perfect-pairing (GVB-PP) wave function $\Psi^{\text{GVB-PP}}$ is composed of N_{gvb} pairs of singlet-coupled local orbitals φ_{i1}, φ_{i2} and a closed-shell core. The perfect-pairing nomenclature refers to the use of only the single valence bond spin coupling among the orbitals.

$$\Psi^{\text{GVB-PP}}=\mathcal{A}[\{\text{core}\}\{\varphi_{11}\varphi_{12}\ldots\varphi_{N_1}\varphi_{N_2}\}\times\{(\alpha\beta-\beta\alpha)\ldots(\alpha\beta-\beta\alpha)\}], \tag{1}$$

with $\mathcal{A}$ the antisymmetrizing operator. The local orbital pairs φ_{i1}, φ_{i2} mutually overlap, however, a strong-orthogonality restriction is applied which forces orbitals of different pairs to be mutually orthogonal. As shown by Goddard *et al.*,[17] this restriction and a computationally more useful form of $\Psi^{\text{GVB-PP}}$ can be represented by expanding each local orbital pair φ_{i1}, φ_{i2} in terms of mutually orthogonal natural orbitals ϕ_{i1}, ϕ_{i2} via the relations,

$$\begin{aligned}\varphi_{i1}&=(\sigma_{i1}^{1/2}\phi_{i1}+\sigma_{i2}^{1/2}\phi_{i2})/(\sigma_{i1}+\sigma_{i2})^{1/2},\\ \varphi_{i2}&=(\sigma_{i1}^{1/2}\phi_{i1}-\sigma_{i2}^{1/2}\phi_{i2})/(\sigma_{i1}+\sigma_{i2})^{1/2},\\ \sigma_{nm}&>0;\quad \sigma_{i1}^2+\sigma_{i2}^2=1,\end{aligned} \tag{2}$$

with the pairwise normalization conditions of the last equation. The natural orbital pairs ϕ_{i1}, ϕ_{i2} are generally well localized between a pair of atoms with ϕ_{i1} of the "bonding" type and ϕ_{i2} having more nodal or "antibonding" character. This simple transformation puts $\Psi^{\text{GVB-PP}}$ into the form,

$$\Psi^{\text{GVB-PP}}=\mathcal{A}[\{\text{core}\}\{(\sigma_{11}\phi_{11}^2-\sigma_{12}\phi_{12}^2)\ldots(\sigma_{N_1}\phi_{N_1}^2-\sigma_{N_2}\phi_{N_2}^2)\}\{\alpha\beta\ldots\alpha\beta\}]. \tag{3}$$

Expansion of this expression shows that $\Psi^{\text{GVB-PP}}$ describing N_{gvb} pairs is an expansion in $2^{N_{\text{gvb}}}$ closed-shell configuration-state functions γ_i, with CI coefficients D_i defined as functionals of the pair coefficients $\{\sigma_{nm}\}$

$$\Psi^{\text{GVB-PP}}=\sum_{i=1}^{2^{N_{\text{gvb}}}} D_i(\{\sigma_{nm}\})\mathcal{A}\left[\left(\prod_k^{N_{\text{gvb}}}\phi_{ik}\phi_{ik}\right)(\alpha\beta\ldots\alpha\beta)\right]=\sum_{i=1}^{2^{N_{\text{gvb}}}} D_i(\{\sigma_{nm}\})\gamma_i. \tag{4}$$

The orbital coefficients $\{\sigma_{nm}\}$ are iteratively solved for Ref. 17 by diagonalizing operators $\mathbf{Y}^i$ for each pair i in the basis of the two natural orbitals ϕ_{i1}, ϕ_{i2} of pair i,

$$\begin{aligned}&\mathbf{Y}^i\boldsymbol{\sigma}_i=\epsilon_i\boldsymbol{\sigma}_i,\\ &Y^i_{nn}=h_{nn}+\frac{1}{2}(nn|nn)+\sum_{k\neq i}\sigma_k^2(2(kk|nn)-(kn|nk)),\\ &Y_{nm}=\tfrac{1}{2}(nm|mn),\quad \text{for } n\neq m.\end{aligned} \tag{5}$$

The sum on k is over orbitals in the other pairs. For the GVB-PP reference, the lowest energy root $(\sigma_{i1},-\sigma_{i2})$ of the two possible roots is selected, with the complementary root of the two-by-two space simply being $(\sigma_{i2},\sigma_{i1})$.

The important point is that the $2^{N_{\text{gvb}}}$ CI coefficients D_i of Eq. (4) are represented in terms of only $2N_{\text{gvb}}$ coefficients $\{\sigma_{nm}\}$. One may refer to this reduction or contraction in the number of variational parameters as an orbital based contraction since the orbital expansion coefficients $\{\sigma_{nm}\}$ define the contraction. For large systems, the iterative determination of these $2N_{\text{gvb}}$ terms σ_{nm} is computationally faster than a diagonalization in the $2^{N_{\text{gvb}}}$ configuration space required for a "linear CI" expansion $\Psi^{\text{linear}}_{\text{gvb}}$ in which the functionals $D_i(\{\sigma_{nm}\})$ of Eq. (4) are replaced by coefficients B_i which have free variational freedom,

$$\Psi^{\text{linear}}_{\text{gvb}}=\sum_{i=1}^{2^{N_{\text{gvb}}}} B_i\gamma_i. \tag{6}$$

Most importantly, as shown below, the GVB-PP wave function and generalizations of the GVB-PP wave function expressed in terms of the $\{\sigma_{nm}\}$ have energies which are nearly identical to that obtained by performing the larger linear CI. This computationally efficient method of treating the closed shell GVB-PP configurations will be shown below to be a very important tool for simplifying configuration expansions generated from a GVB-PP reference. Aside from these computational issues, the GVB wave function also has the important conceptual advantage that the local orbital representation allows for a compact, chemically interpretable wave function.

III. RESTRICTED CONFIGURATION INTERACTION FROM A GVB-PP REFERENCE

The RCI wave function is generated from the GVB-PP wave function by allowing for the open-shell spatial occupation $\phi_{i1}\phi_{i2}$ in each pair in addition to the two closed-shell GVB-PP occupations ϕ_{i1}^2 and ϕ_{i2}^2. In addition, for a given spin eigenstate, the various spin couplings among the open-shell pairs are accounted for. The RCI wave function is thus a general multiconfigurational reference wave function which can both dissociate properly and account for general spin eigenstates. It has recently been shown[5] that, as a reference wave function for multiconfigurational perturbation theory, the RCI wave function gives results comparable to results obtained[6] with the much larger complete-active-space (CASSCF) reference wave function.

The RCI expansion we have formulated is constructed making intrapair excitations explicitly from the GVB-PP wave function of Eq. (3). This is in contrast to the RCI wave function previously constructed by others[13,16] by making excitations from the linear CI expansion of the GVB-PP wave function [Eq. (6)]. Furthermore, following a suggestion of Ref. 18, we have found that an accurate approximation is to limit the number of excitations from the GVB-PP reference. By using the computational efficiencies of the GVB-PP reference discussed above, we presently show that a computationally efficient RCI wave function can be defined which allows for the correlation of a large number of GVB pairs.

We first focus on the spatial aspects of the RCI wave function. The three possible spatial states of an "RCI pair" i are defined as the GVB state ξ_{i0} and the two other pair states ξ_{i1}, and ξ_{i2} which together form the orthogonal complement to ξ_{i0},

$$\begin{aligned} &\xi_{i0}=\sigma_{i1}\phi_{i1}^2-\sigma_{i2}\phi_{i2}^2 \quad \text{(GVB-PP)},\\ &\xi_{i1}=\phi_{i1}\phi_{i2}; \quad \xi_{i2}=\sigma_{i2}\phi_{i1}^2+\sigma_{i1}\phi_{i2}^2. \end{aligned} \tag{7}$$

In the GVB-PP wave function all pairs are in the ξ_{i0} state. The ξ_{i1} pair state is of the open-shell form and is orthogonal to ξ_{i0} via orthogonality of the natural orbitals. The ξ_{i2} state forms the other complement to ξ_{i0} with complementarity in this case defined with respect to the pair coefficient space $\boldsymbol{\sigma}_i=(\sigma_{i1},\sigma_{i2})$. As discussed above [Eq. (5)], the optimization of the GVB-PP $\boldsymbol{\sigma}_i$ gives two roots per pair, the GVB-PP root $(\sigma_{i1},-\sigma_{i2})$ and the complementary root $(\sigma_{i2},\sigma_{i1})$. The ξ_{i2} pair state is formed from this complementary $\boldsymbol{\sigma}_i$ solution. The ξ_{i2} effectively adjust the $\boldsymbol{\sigma}_i$ coefficients of ξ_{i0} due to the presence of the ξ_{i1} excitations in the RCI expansion.

In general, the RCI wave function constructed from a GVB-PP wave function of N_p pairs, will allow only N_{rci} of these pairs to be correlated beyond GVB-PP by occupation of all three of the possible pair states ξ_{ij}. The remaining $N_{\text{gvbmf}}=(N_p-N_{\text{rci}})$ pairs are forced to stay in the GVB-PP ξ_{i0} state. This restriction allows for correlation of a region of the system beyond the reference GVB-PP level, in the field of the remaining GVB-PP pairs. The utility of such a local specification of higher correlation is evident in many chemical problems such as correlation of dissociating bonds in the GVB-PP field of the unperturbed bonds. In addition, we show below that the nature of the GVB-PP expansion allows for the N_{gvbmf} GVB-PP pairs to be effectively represented as a single-particle mean field. Hence the nomenclature N_{gvbmf} represents those pairs generating this GVB-PP mean field.

A spatial amplitude Φ_r^{RCI} contributing to the Ψ^{RCI} wave function has the specified form,

$$\Phi_r^{\text{RCI}}=\{\text{core}\}\left(\prod_{i=1}^{N_{\text{gvbmf}}}\xi_{i0}\right)\left(\prod_{j=1}^{N_{\text{rci}}}\xi_{jn}\right) \quad n=0,1,2, \tag{8}$$

where the specific spatial term Φ_r^{RCI} is distinguished by the states ($n=0$, 1, 2) of the N_{rci} pairs and {core} denotes a closed-shell core. For N_{rci} pairs it is possible to generate $3^{N_{\text{rci}}}$ such spatial terms Φ_r^{RCI}. However, we show below that it is possible to identify a subset of these spatial terms which are the most energetically important. This subset is specified by allowing a maximum number of excited pair states (ξ_{i1} or ξ_{i2}) to occur in any Φ_r^{RCI}.

Having specified the spatial terms Φ_r^{RCI}, configuration state functions ψ_n^{RCI} defining Ψ^{RCI} can be specified by assigning all possible spin eigenfunctions Θ_k to the spatial terms Φ_r^{RCI},

$$\psi_n^{\text{RCI}}=\mathscr{A}[\Phi_r^{\text{RCI}}\Theta_k], \tag{9}$$

The number of Θ_k assigned to a Φ_r^{RCI} increases as a function of the number of ξ_{i1} open-shell RCI pairs in Φ_r^{RCI} in the usual[19] fashion. The RCI wave function is now completely specified as an expansion in the configuration state functions ψ_n^{RCI} with variational weights C_n,

$$\Psi^{\text{RCI}}=\sum_n C_n\psi_n^{\text{RCI}}. \tag{10}$$

Thus the RCI expansion is expressed in terms of configurations which are identified by the specific pairs which are excited beyond the GVB-PP level ξ_{i0}, and the spin coupling among the open-shell ξ_{i1}.

A very important and novel aspect of Ψ^{RCI} is the so-called contracted nature of the expansion. The RCI wave function is contracted in the sense that each variationally weighted entity ψ^{RCI} is in fact a sum of up to $2^{N_{\text{gvb}}}$ individual uncontracted configuration state functions γ_i. The contraction of a given configuration is explicitly shown below,

TABLE I. The number of contracted RCI configurations $N_{\text{con}}^{\text{RCI}}$ vs the number of uncontracted configurations N_{ucon} contained in Ψ^{RCI} with N_{rci} pairs.

N_{rci}	$N_{\text{con}}^{\text{RCI}}$	N_{ucon}
4	99	136
6	388	1536
8	997	13 824
10	2046	105 984
12	3655	727 040
14	5944	4603 904

$$\psi_n^{\text{RCI}} = \mathscr{A}[\Phi_r^{\text{RCI}}\Theta_k] = \mathscr{A}\left[\left(\prod_{j=1}^{N_p}\xi_{jp}\right)\Theta_k\right]$$

$$= \sum_m A_m(\{\sigma\})\mathscr{A}\left[\left(\prod_s \phi_{ns}\right)\Theta_k\right]$$

$$= \sum_m A_m(\{\sigma\})\gamma_m . \tag{11}$$

This explicitly shows the RCI configuration ψ_n^{RCI} as a weighted sum of order 2^{N_P} individual configurations labeled γ_m. This contraction of a given configuration is analogous to the orbital based contraction discussed above for GVB-PP. In conventional "linear" CI the γ_m are the basis in which CI is performed. The contracted CI contains this full γ_m basis but does not allow each γ_m to independently vary. Instead, fixed linear combinations of the γ_m vary as specified by the coefficients $A_m(\{\sigma\})$. The computational significance of this statement is that Ψ^{RCI} can be determined in a space with a dimension which is much smaller than the number of individual γ_m contained in the expansion. To illustrate this large reduction in dimensionality afforded by the contraction procedure, we have tabulated in Table I the number of contracted RCI configurations vs the number of uncontracted configurations γ_m in Ψ^{RCI} for $N_p = N_{\text{rci}} = 4$, 14 pairs. A singlet state was assumed and a limit of at most three non-GVB-PP pair states (ξ_{i1} or ξ_{i2}) in any ψ_n^{RCI} was imposed. The corresponding restriction of at most six open-shell orbitals (three open-shell pairs) was imposed on the uncontracted expansion.

The dimension of the contracted space clearly grows with N_{rci} at a much slower rate than that of the uncontracted space. This slow growth of the contracted space is a prerequisite to correlating much larger systems than previously possible. To realize this potential it is also necessary to demonstrate an efficient scheme for calculating matrix elements among contracted RCI configurations, this is the topic of the next section. Second, we must address the accuracy of the contraction scheme relative to CI in the corresponding uncontracted space generated with the same restriction on the maximal number of open-shell orbitals as in the contracted RCI. Relative to this analogous uncontracted CI, the contraction scheme clearly involves the orbital based contraction approximation analogous to the GVB-PP case. Second, by placing an upper limit on the number of ξ_{i2} pair excitations, the contraction scheme is limiting the extent of reoptimization of the GVB pair coefficients $\{\sigma_{nm}\}$ caused by the open-shell ξ_{i1} excitations. Test calculations presented below indicate that the contracted CI is indeed a very good approximation to the uncontracted CI.

It is important to distinguish the contraction method outlined here with the contraction method traditionally used in multireference CI calculations.[2] The latter multireference CI contraction is based on making excitations from an uncontracted MCSCF wave function with the resulting contracted CI coefficients being functionals of the uncontracted MCSCF CI coefficients. In contrast, our contraction method is based on both making excitations from the GVB-PP reference *and* from the fact that the GVB-PP CI coefficients are contracted functions of the orbital expansion coefficients $\{\sigma_{nm}\}$. This latter orbital based contraction of the closed-shell space proves to be very important for efficient generation of matrix elements among contracted RCI configurations and, as shown above, for reducing the length of the CI expansion.

IV. CONTRACTED RCI MATRIX ELEMENTS USING GVB-PP MEAN FIELDS

Since each contracted RCI configuration contains a sum of up to 2^{N_P} uncontracted configurations, the calculation of Hamiltonian matrix elements among contracted RCI configurations could potentially require an expensive computation of many uncontracted matrix elements. Fortunately, the calculation of matrix elements among contracted RCI configurations is greatly simplified by the realization that the common nonexcited GVB-PP parts of two interacting configurations can be replaced by a single-particle Coulomb-exchange mean field operator. This simplification involves no further approximations beyond those made in the definition of the contracted RCI expansion. We presently discuss the details of contracted matrix element evaluation utilizing this GVB mean field procedure.

A. Correlation in a GVB-PP mean field

The simplest demonstration of this mean field approach considers the treatment of the N_{gvbmf} unexcited GVB pairs in the RCI configurations of Eqs. (8) and (9). It is possible to write each contracted configuration ψ_n^{RCI} as an antisymmetrized product of the GVB-PP wave function Ψ^{gvbmf} which is common to all configurations ψ_n^{RCI}, multiplied by the remaining part of the configuration, $\psi_n^{N_{\text{rci}}}$, describing the N_{rci} pairs correlated beyond GVB-PP,

$$\psi_n^{\text{RCI}} = \mathscr{A}[\Psi^{\text{gvbmf}}\psi_n^{N_{\text{rci}}}];$$

$$\Psi^{\text{gvbmf}} = \mathscr{A}\left[\left(\prod_{i=1}^{N_{\text{gvbmf}}}\xi_{i0}\right)(\alpha\beta\ldots\alpha\beta)\right], \tag{12}$$

$$\psi_n^{N_{\text{rci}}} = \mathscr{A}[\Phi_r^{N_{\text{rci}}}\Theta_k].$$

In these equations Ψ^{gvbmf} and $\psi_n^{N_{\text{rci}}}$ are defined in the space of the $2N_{\text{gvbmf}}$ and $2N_{\text{rci}}$ coordinates, respectively. The antisymetrizer of ψ_n^{RCI} permutes between these sets of coordinates. Since Ψ^{gvbmf} is common to all configurations, Ψ^{RCI} can be factorized into Ψ^{gvbmf} and the expansion in the space of N_{rci} pairs, $\Psi^{N_{\text{rci}}}$,

$$\Psi^{\mathrm{RCI}}=\mathscr{A}[\Psi^{\mathrm{gvbmf}}\Psi^{N_{\mathrm{rci}}}];\quad \Psi^{N_{\mathrm{rci}}}=\sum_n C_n\psi_n^{N_{\mathrm{rci}}}. \tag{13}$$

This factorization is possible since Ψ^{gvbmf} and $\Psi^{N_{\mathrm{rci}}}$ do not share any common spatial orbitals. Furthermore, the CI coefficients C_n of Eq. (13) are the same as those of Eq. (4) since Ψ^{gvbmf} is normalized independently of $\Psi^{N_{\mathrm{rci}}}$ by the pairwise normalization of a GVB-PP wave function [Eq. (2)].

Using this factorization and the fact that Ψ^{gvbmf} is a weighted sum of closed shell determinants [Eq. (4)], a straightforward generalization of the hypothetical limit in which Ψ^{gvbmf} is a single determinant gives the following simplified energy expression for Ψ^{RCI},

$$\langle\Psi^{\mathrm{RCI}}|\mathscr{H}|\Psi^{\mathrm{RCI}}\rangle=\langle\Psi^{\mathrm{gvbmf}}|\mathscr{H}|\psi^{\mathrm{gvbmf}}\rangle + \langle\Psi^{N_{\mathrm{rci}}}|\mathscr{H}^*|\Psi^{N_{\mathrm{rci}}}\rangle. \tag{14}$$

The first matrix element is the GVB-PP energy of Ψ^{gvbmf} and the second matrix element is the energy of $\Psi^{N_{\mathrm{rci}}}$ evaluated with a new effective Hamiltonian $\mathscr{H}^*$. This effective Hamiltonian contains the full Hamiltonian $\mathscr{H}$ and the generalized Fock operator[3,20] F^{gvbmf} of Ψ^{gvbmf},

$$\mathscr{H}^*=\mathscr{H}+F^{\mathrm{gvbmf}};\quad F^{\mathrm{gvbmf}}=\sum_m \sigma_m^2(2J_{mm}-K_{mm}). \tag{15}$$

The F^{gvbmf} single-particle operator is simply a weighted sum of closed-shell Fock operators for orbitals m contained in Ψ^{gvbmf}. Computationally, F^{gvbmf} can be treated as a single conventional closed-shell Fock operator in the atomic orbital space using the closed-shell single-particle atomic-orbital density matrix of Ψ^{gvbmf}.

This derivation conceptually and computationally extends the traditional approach of correlating a spatial region in a surrounding Hartree–Fock mean field to the use of a *correlated* GVB-PP mean field. This GVB mean field significantly reduces the computational effort of the RCI calculation by replacing the $2^{N_{\mathrm{gvbmf}}}$ set of configurations in Ψ^{gvbmf} by one single-particle operator. The two-electron part of the Hamiltonian is therefore effectively reduced to the space of the $2N_{\mathrm{rci}}$ coordinates. Calculations presented below show that F^{gvbmf} accurately represents the effects of an uncontracted expansion in $2^{N_{\mathrm{gvbmf}}}$ configurations multiplying the expansion $\Psi^{N_{\mathrm{rci}}}$.

B. Matrix elements in the RCI space

Given that we have effectively integrated the static or unexcited Ψ^{gvbmf} space out of the correlation problem, the remaining problem is to efficiently formulate the matrix elements in the excited RCI space between the $\psi_n^{N_{\mathrm{rci}}}$ contracted configurations. We presently describe how the efficiencies of the GVB mean field approach can be extended to the construction of contracted matrix elements in the RCI space.

The nonzero matrix elements between configurations $\psi_n^{N_{\mathrm{rci}}}$ and $\psi_m^{N_{\mathrm{rci}}}$ of Eq. (12) can be classified in the usual fashion[21] based upon the difference between the contracted spatial configurations $\Phi_n^{N_{\mathrm{rci}}}$ and $\Phi_m^{N_{\mathrm{rci}}}$. The four classes of matrix elements are: (a) The diagonal case where $\Phi_n=\Phi_m$, (b) the class for which Φ_n and Φ_m differ by an intrapair single excitation, e.g., Φ_n is in the ξ_{j0} state and Φ_m in the ξ_{j1} state, (c) the case when Φ_n and Φ_m differ by an intrapair double excitation, and (d) the case when Φ_n and Φ_m differ by intrapair single excitations at two pair sites. The RCI Hamiltonian is made relatively sparse by the fact that the RCI pairs do not share common natural orbitals and by the intrapair nature of the RCI excitations.

Since the $\psi_n^{N_{\mathrm{rci}}}$ are composed of up to $2^{N_{\mathrm{rci}}}$ uncontracted configurations, it is too expensive to simply expand each configuration into uncontracted configurations and then sum matrix elements among uncontracted configurations. The key to avoiding this $2^{N_{\mathrm{rci}}}$ growth in computational labor is once again the use of the GVB mean field approach, and the imposition of a limit on the maximum number of excitations from the GVB ξ_{i0} state in the space of RCI pairs. For the first three classes of matrix elements between configurations $\psi_n^{N_{\mathrm{rci}}}$ and $\psi_m^{N_{\mathrm{rci}}}$ listed above the following approach is adopted. The first step is to identify the set of N_{nm}^0 pairs in the interacting spatial configurations $\Phi_n^{N_{\mathrm{rci}}}$ and $\Phi_m^{N_{\mathrm{rci}}}$ which are in the GVB-PP state ξ_{i0} in both $\Phi_n^{N_{\mathrm{rci}}}$ and $\Phi_m^{N_{\mathrm{rci}}}$. The remaining $N_{nm}^{\mathrm{ex}}=(N_{\mathrm{rci}}-N_{nm}^0)$ excited pairs must satisfy the condition that the pairs are in the excited ξ_{i1} or ξ_{i2} state in $\Phi_n^{N_{\mathrm{rci}}}$ and/or $\Phi_m^{N_{\mathrm{rci}}}$. As in the analysis of the static GVB mean field above we now rewrite $\psi_{n,m}^{N_{\mathrm{rci}}}$ with their common GVB-PP space of N_{nm}^0 pairs factored out into a GVB-PP wave function $\psi_{nm}^{\mathrm{gvbmf}}$ and into the remaining excited terms ψ_n^{ex} and ψ_m^{ex} defined in the defined in the space of N_{nm}^{ex} pairs,

$$\psi_n^{N_{\mathrm{rci}}}=\mathscr{A}[\psi_{nm}^{\mathrm{gvbmf}}\psi_n^{\mathrm{ex}}];\quad \psi_m^{N_{\mathrm{rci}}}=\mathscr{A}[\psi_{nm}^{\mathrm{gvbmf}}\psi_m^{\mathrm{ex}}] \tag{16}$$

$$\psi_{nm}^{\mathrm{gvbmf}}=\mathscr{A}\left[\left(\prod_{i=1}^{N_{nm}^0}\xi_{i0}\right)(\alpha\beta\ldots\alpha\beta)\right];$$

$$\psi_n^{\mathrm{ex}}=\mathscr{A}[\Phi_n^{N_{\mathrm{ex}}}\Theta_k]. \tag{17}$$

The $\Phi_n^{N_{\mathrm{ex}}}$ and Θ_k spatial and spin terms defining the reduced configurations ψ_n^{ex} are defined in the space of the N_{nm}^{ex} contracted pairs. In a manner analogous to the derivation of F^{gvbmf} it is readily shown that the following expression applies to the matrix element between $\psi_n^{N_{\mathrm{rci}}}$ and $\psi_m^{N_{\mathrm{rci}}}$,

$$\langle\psi_{nm}^{\mathrm{gvbmf}}\psi_n^{\mathrm{ex}}|\mathscr{H}^*|\psi_{nm}^{\mathrm{gvbmf}}\psi_m^{\mathrm{ex}}\rangle=\delta_{nm}\langle\psi_{nm}^{\mathrm{gvbmf}}|\mathscr{H}^*|\psi_{nm}^{\mathrm{gvbmf}}\rangle + \langle\psi_n^{\mathrm{ex}}|\mathscr{H}_{nm}^*|\psi_m^{\mathrm{ex}}\rangle, \tag{18}$$

where the effective Hamiltonian $\mathscr{H}_{nm}^*$ is given by,

$$\mathscr{H}_{nm}^*=\mathscr{H}^*+F_{nm}^{\mathrm{gvbmf}};\quad F_{nm}^{\mathrm{gvbmf}}=\sum_q \sigma_q^2(2J_{qq}-K_{qq}). \tag{19}$$

The orbitals q are those defining $\psi_{nm}^{\mathrm{gvbmf}}$ and $\mathscr{H}^*$ includes the static GVB Fock operator of Eq. (15). The single-particle Fock operator F_{nm}^{gvbmf} effectively represents the GVB-PP mean field common to ψ_n^{RCI} and ψ_m^{RCI}.

The evaluation of the contracted RCI matrix element has therefore been reduced to the space of N_{nm}^{ex} contracted RCI pairs using $\mathscr{H}_{nm}^*$. The matrix element in the N_{nm}^{ex} space is of

one of the four classes noted above with, by definition, the difference between spatial terms $\Phi_n^{N_{\rm rci}}$ and $\Phi_m^{N_{\rm rci}}$ occurring at one or two of the $N_{nm}^{\rm ex}$ pair sites. The matrix element in the $N_{nm}^{\rm ex}$ space is,

$$\langle \psi_n^{\rm ex}|\mathcal{H}_{nm}^*|\psi_m^{\rm ex}\rangle = \langle \xi_1^n \cdots \xi_{N_{nm}^{\rm ex}}^n \Theta_r|\mathcal{H}_{nm}^*|\mathcal{A}[\xi_1^m \cdots \xi_{N_{nm}^{\rm ex}}^m \Theta_s]\rangle. \tag{20}$$

Since the pair functions ξ_{ij} are orthonormal, this contracted matrix element can be evaluated in the same manner as an uncontracted matrix element. However, interactions involving ξ_{i0} and ξ_{i2} require additional summations over the two closed-shell orbitals of these pair functions. The net matrix element is a sum of uncontracted matrix elements weighted by products of $\{\sigma_{nm}\}$ coefficients. Note however that the class (c) type of uncontracted matrix element involves a difference of diagonal matrix elements and hence requires, unlike the uncontracted case, the evaluation of $F_{nm}^{\rm gvbmf}$ while the contracted matrix element of type (d) involves, as in the uncontracted case, no one-particle component.

In summary, by using the GVB mean field approach the two-electron part of contracted matrix elements has been effectively reduced to the space of $N_{nm}^{\rm ex}$ pairs. Furthermore, since we have a limit of order three on the number of non-GVB pairs in a given configuration, the maximum size of the $N_{nm}^{\rm ex}$ space is of order six pairs and on average $N_{nm}^{\rm ex}$ is two to three pairs. Thus the cost of evaluating the sums of uncontracted two-electron matrix elements in Eq. (20) is significantly reduced by this reduction in the size of the $N_{nm}^{\rm ex}$ space.

V. PSEUDOSPECTRAL INTEGRAL EVALUATION

The RCI matrix elements discussed above can be expressed in terms of the Coulomb and exchange operators J_{ij} and K_{ij} where i,j refer to the three possible orbital products of each RCI pair, $\phi_{i1}\phi_{i1}$, $\phi_{i2}\phi_{i2}$, $\phi_{i1}\phi_{i2}$. The matrix elements of these operators between atomic basis functions χ_μ, χ_ν, have the usual form,

$$\begin{aligned}\langle \mu|J_{ij}|\nu\rangle &= (\mu(1)\nu(1)|\phi_i(2)\phi_j(2));\\ \langle \mu|K_{ij}|\nu\rangle &= (\mu(1)\phi_i(1)|\nu(2)\phi_j(2)).\end{aligned} \tag{21}$$

The pseudospectral representation of a Coulomb matrix element is represented by,

$$\langle \mu|J_{ij}|\nu\rangle = \sum_g Q_\mu(g) J_{ij}(g) R_\nu(g). \tag{22}$$

The sum is over grid points g. $J_{ij}(g)$ is the physical space representation of J_{ij} given by a sum of three-center, one-electron integrals weighted by the orbital expansion coefficients c_k^i

$$J_{ij}(g) = \sum_{kl} c_k^i c_l^j \int \frac{\chi_k(1)\chi_l(1)}{r_{1g}}\, d\mathbf{r}_1. \tag{23}$$

The term $R_\nu(g)$ is simply the basis function at grid point g, $\chi_\nu(g)$. Finally, the term $Q_\mu(g)$ results from the least squares fit of $J_{ij}(g)\chi_\nu(g)$ to the atomic orbital basis augmented by a dealiasing basis. Similar expressions apply to the exchange operator. Further details regarding the the construction of the pseudospectral quantities can be found in Refs. 7–12. To attain higher accuracy, a limited number of two-electron integrals contributing to $J_{ij}^{\mu\nu}$ and $K_{ij}^{\mu\nu}$ are evaluated analytically as discussed in Ref. 11.

Using $N_{\rm bas}$ basis functions $\{\chi\}$ in which to expand the orbitals ϕ_i, the pseudospectral evaluation of each Coulomb and exchange operator over this basis scales as $N_{\rm bas}^3$ as compared to the conventional analytic scaling of $N_{\rm bas}^4$. Second, the formation of the RCI matrix elements requires that the Coulomb and exchange operators be transformed from the atomic basis $J_{ij}^{\mu\nu}$ to the natural orbital basis J_{ij}^{kl} by a simple two-index transform,

$$\langle \phi_k|J_{ij}|\phi_l\rangle = \sum_{\mu\nu} c_\mu^k c_\nu^l J_{ij}^{\mu\nu}. \tag{24}$$

This two-index transformation thus avoids the expensive conventional four-index transform from the integrals over basis functions to integrals over orbitals which is a major bottleneck (an $N_{\rm bas}^5$ procedure) in conventional MCSCF and CI approaches.

VI. TEST RESULTS

In the following sections we are primarily interested in demonstrating the accuracy of the pseudospectral contracted RCI expansion relative to the corresponding conventional uncontracted expansion. In addition we present some representative examples of the improvements in spectroscopic parameters obtained by RCI relative to GVB-PP. Finally we discuss the computational speed of the RCI program for larger problems.

A. Details of calculations

The self-consistent pseudospectral GVB-PP calculations were performed with the PS-GVB program of Ref. 12. The contracted pseudospectral RCI program was written in a direct-CI manner to iteratively[22] diagonalize the full Hamiltonian over contracted RCI configurations. The main task of the RCI program is to generate matrix-vector products of contracted RCI matrix elements. The pseudospectral RCI integrals of Eq. (22) were produced by a modification of the PS-GVB program. All contracted RCI results used a maximum of three pair excitations from the GVB-PP reference. The uncontracted pseudospectral RCI calculations were done with the uncontracted version of the contracted code while the uncontracted RCI calculations using all analytic integrals were done with the programs of Ref. 23.

The RCI calculations were performed with the so-called "ultra-fine" grid of the PS-GVB program. This grid has approximately 425 points per atom. Analytic atom and diatomic corrections were used as explained in Ref. 11. We have found that it is possible to limit these corrections of the matrix elements involving a GVB pair to basis functions on the two atoms defining the pair. This intrapair correction approach is currently implemented for the GVB Coulomb and exchange matrix elements and the RCI exchange matrix elements in the CPU timings below.

TABLE II. Convergence of RCI energy with maximum open-shell occupation.

Molecule	Maximum open-shell pairs 2	3	4	5	6
	E(GVB-PP)-*E*(RCI) (a.u.)				
N_2	0.068 045	0.068 088	0.068 604	0.068 604	...
Ethane	0.028 991	0.029 018	0.029 191	0.029 191	0.029 191
CH_3CN	0.067 121	0.079 295	0.079 575	0.079 586	0.079 602
Glyoxal	0.051 784	0.051 814	0.052 464	0.052 464	0.052 466
Ethanol	0.026 867	0.026 892	0.027 034	0.027 034	0.027 034

The tests of the contracted method used 631G** basis sets. The diatomic calculations in Sec. VI E used correlation consistent[24] $4s3p2d$ basis sets on C,N,O and a $3s2p$ set on H.

B. Test of open-shell restriction

As discussed in Sec. IV B, the computational cost of the RCI expansion can be significantly reduced by restricting the maximum number of contracted pair excitations to a maximum level, nopmx, within any configuration. The corresponding statement in the uncontracted CI is that we limit the CI to at most 2* nopmx open-shell orbitals. This restriction in the contracted expansion not only places the same limit on the maximum open-shell occupation, but also limits the reoptimization of the pair coefficients $\{\sigma\}$ since the maximum number of ξ_{i2} pairs is also nopmx. As discussed above this restriction is one of the main approximations of the contraction method. In this section we present uncontracted RCI results for some small systems to support a limit on the open-shell occupations. The results of the next section comparing contracted and uncontracted results will test the remaining approximations of a limit on the ξ_{i2} type excitations and the accuracy of the orbital based contraction.

The convergence of the uncontracted RCI energy with maximum number of open-shell pairs is shown in Table II for some small molecules. All valence pairs were correlated except for the ethanol OH bond due to limitations of the uncontracted CI program. In some cases most or all of the extra configurations generated by a larger open shell number do not have the correct symmetry and hence the RCI energy does not change appreciably. For this reason the CH_3CN molecule with the lowest symmetry is perhaps the best example. The use of three open shell pairs recovers 98% or more of the six open-shell RCI correlation energy relative to GVB-PP while four open-shell pairs is nearly indistinguishable from six. From these results and others[18] it is plausible to assume that for organic molecules near their equilibrium geometries that at most three or four open-shell pairs in any given configuration yield sufficient accuracy.

C. Accuracy of contraction

The accuracy of the pseudospectral contracted RCI expansion was calculated relative to the corresponding uncontracted RCI expansion for the molecules in Table III using a self-consistent GVB-PP reference obtained pseudospectrally.

TABLE III. Accuracy of contracted RCI relative to uncontracted RCI. ΔE is the energy difference between the contracted and uncontracted wave functions. N_{pair} is the number of RCI pairs correlated.

Molecule	N_{pair}	ΔE (kcal/mol)
H_2O	4	0.014
C_2H_2	5	0.018
C_2H_4	6	0.022
C_2H_6	7	0.047
Glyoxal	7	0.049
Acetic acid	8	0.034
Ethanol	8	0.046
Acetone	10	0.005

The contracted RCI was performed with a restriction of at most three pair excitations relative to the GVB-PP reference. The uncontracted RCI used the pseudospectral RCI integrals and a maximum open-shell occupation of three pairs. As discussed above, the contracted expansion contains all of the configurations of the uncontracted expansion. This comparison tests the approximations of the contraction procedure, namely the restricted reoptimization of the GVB-PP $\{\sigma\}$ parameters in the presence of the open-shell pair excitations and the accuracy of the orbtal based contraction.

For up to ten pairs the difference between the contracted and uncontracted RCI energies is seen to be negligible. Tests on systems larger than ten pairs were not attempted due to the unmanagable lengths of the uncontracted RCI expansion for larger pair number. However, there is no apparent growth in the contracted–uncontracted energy difference with pair number for these examples. These results indicate that the approximations made in the contracted method are indeed very reliable.

D. Accuracy of pseudospectral integration

Hartree-Fock and GVB-PP wave functions evaluated pseudospectrally with limited one- and two-center analytic integral corrections have been previously shown[11] to have errors of order 0.01–0.04 kcal/mol relative to the corresponding all analytic integral calculations. We presently show that a similar accuracy applies to the pseudospectral RCI integral evaluation. Table IV presents a comparison between GVB-PP and uncontracted RCI calculations with all analytic integral evaluation vs pseudospectral integral evaluation. The error incurred by the pseudospectral evaluation of the RCI integrals is clearly very small, of order 0.05 kcal/mol. It should be noted that this accuracy of the pseudospec-

TABLE IV. Accuracy of pseudospectral RCI integration. Uncontracted analytic RCI energies *E*(AN-RCI) vs uncontracted pseudospectral energies *E*(PS-RCI) (a.u.).

Molecule	*E*(AN-RCI)	*E*(PS-RCI)	Δ (kcal/mol)
C_2H_4	−78.167 882	−78.167 917	0.022
C_2H_6	−79.372 059	−79.372 058	0.001
Ethanol	−154.256 560	−154.256 470	0.056
Glyoxal	−226.785 405	−226.785 358	0.030
Acetic acid	−228.002 985	−228.002 988	0.002

TABLE V. GVB-PP and RCI bond lengths (Å) and harmonic frequencies (cm^{-1}).

Molecule	GVB R_e	RCI R_e	Expt. R_e	GVB ω_e	RCI ω_e	Expt. ω_e
CO	1.119	1.129	1.128	2331	2179	2170
F_2	1.485	1.422	1.413	675	856	917
N_2	1.092	1.098	1.098	2413	2388	2359

tral method is only obtainable by using the limited set of analytic corrections in the pseudospectral procedure. Recent pseudospectral calculations[25] of CI and MP2 energies without such corrections gave non-negligible differences of order 0.7 kcal/mol from the analytic results. We have found that the corrections of integrals involving orbitals of a GVB pair can be limited to basis functions on the two atoms defining the GVB pair.

E. Diatomic tests, RCI properties

In addition to the above construction of an efficient RCI methodology for large molecules, an equally important task is to understand the quality of this wave function for predicting molecular properties. As a preliminary step in this direction we present some representative examples of the improvements in diatomic potential parameters obtained by RCI relative to GVB-PP. Lacking RCI gradient capabilities at this time we are limited to these simple examples. Table V presents the GVB-PP and RCI potential parameters for multiply bonded molecules CO, N_2, and F_2. The RCI wave function clearly corrects the substantial errors made by GVB-PP.

A more thorough study of the predictive properties of the RCI wave function will be the focus of future work. Some other representative uncontracted RCI calculations by Goddard *et al.* can be found in Refs. 13 and 16. In general, we expect that it will be necessary to go beyond the RCI approximation to reliably obtain quantitative accuracy for molecular observables including dissociation energies and van der Waals interactions which are know to require high levels of correlation. In particular, we intend to use the RCI wave function as a general reference to be corrected by generalized Møller–Plesset perturbation theory. This multiconfigurational perturbation theory from an RCI or CASSCF wave function has recently been shown[3–6] to be a very accurate and computationally efficient approach. In addition it has been shown[5] that generalized Møller–Plesset observables calculated with an RCI reference are comparable to those obtained with the much larger CASSCF reference.[6]

F. Timings

To provide a scale for the computational requirements of the GVB-RCI method we have performed calculations on the molecules in Table VI involving up to 35 GVB-RCI pairs and 250 basis functions. The GVB computations and RCI integrals were performed on an IBM-370 work station while the RCI energy was calculated on an IBM-580 which is roughly 1.5 times as fast as the IBM-370 for this code. All GVB integrals and RCI exchange integrals were done with a limited set of intrapair analytic corrections. To converge the GVB energy to 5×10^{-5} hartrees requires from 10 to 13 iterations for these examples. The GVB time is dominated by the integral evaluation. Normalizing the GVB CPU times linearly with respect to the number of GVB pairs and the number of iterations to convergence, the GVB CPU time displays an $N_{\rm bas}^{2.5}$ scaling. The RCI integration time has a nearly equivalent scaling. The RCI energy evaluation time is well within the time required to evaluate the RCI integrals. The RCI energy calculation time scales with the number of RCI pairs $N_{\rm rci}$ approximately as $N_{\rm rci}^{3.8}$, however, this is a preliminary result as the RCI energy code requires further optimization.

TABLE VI. CPU times (minutes) for self-consistent GVB (T-GVB), RCI integral evaluation (T-RCINT), and RCI energy evaluation (T-ERCI) for molecules with $N_{\rm bas}$ basis functions and $N_{\rm pair}$ electron pairs. $N_{\rm con}$ is the number of contracted RCI configurations.

Molecule	$N_{\rm bas}$	$N_{\rm pair}$	T-GVB	T-RCINT	T-ERCI	$N_{\rm con}$
Dimet. glyoxal	120	17	41	20	3	10915
Alanine	160	23	140	50	10	14428
Leucine	200	26	310	115	13	40678
Arginine	250	35	650	224	60	101221

Although the CPU times can certainly be reduced by further optimization, it is apparent from these examples that the pseudospectral GVB-RCI method can be applied to large molecules within manageable CPU times. It is important to stress that for many applications one would not need to correlate all pairs of a molecule but rather a small subset of pairs involved in changes from an initial to final state. The local nature of the GVB pairs greatly simplifies the assignment of the chemically important pairs.

VII. CONCLUSION

In conclusion, pseudospectral integral evaluation combined with a novel GVB based contracted CI method has been shown to be a feasible approach for performing large correlated calculations within manageable CPU times. Much work remains to be done in both the optimization of the current approaches and in their extension to more accurate methods correlation. We intend to extend the contracted CI procedure to the generalized Møller–Plesset theory using the contracted RCI wave function as a reference. Such a generalized Møller–Plesset theory is optimally implemented within the pseudospectral formalism in conjunction with the local virtual orbital methodology of Pulay.[26] One of the most important conclusions to be drawn from this and related works is that an essential computational and conceptual simplifying element of all of these methods is the use of a local orbital basis.

ACKNOWLEDGMENTS

This research was supported by grants from NSF and NIH. M. N. R. thanks NIH for SBIR Grant No. 2 R44 GM46160-02.

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